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Enzymic deacetylation of derivatives of 1,2-*O*-isopropylidene-α-D-hexofuranoses

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ABSTRACT

Enzymically catalysed, partial deacetylation of the 5,6-diacetates of 3-deoxy-1,2-*O*-isopropylidene-α-D-*ribo*-hexofuranose and 1,2-*O*-isopropylidene-α-D-gluco- and -allo-furanose with different substituents at C-3 (OAc, OMe, NHAc) gives the 5-acetate, which migrates rapidly to give the 6-acetate. The initial rate of deacetylation depends on the size of the 3-substituent and the configuration at C-3.

INTRODUCTION

In continuing studies of the use of enzymes in the transformation of carbohydrate derivatives[1], we have investigated the selective hydrolysis of the 5,6-diacetates of 1,2-*O*-isopropylidene-α-D-hexofuranose derivatives with different 3-substituents and configuration at C-3.

The chemical deacetylation of carbohydrate acetates in both aqueous acid[2] and alkaline[3] media can be accompanied by acetyl migration from secondary to primary hydroxyl groups, and we have investigated this phenomenon under the neutral conditions of enzyme catalysis.

EXPERIMENTAL

General. — Melting points were determined on a Kofler block and are not corrected. Optical rotations were determined with an Opton Photoelectric Precision Polarimeter at 20°. The ^{1}H- (400 MHz) and ^{13}C-n.m.r. (100 MHz) spectra were obtained with a Bruker AM instrument at 27° on solutions in $CDCl_3$ (internal Me_4Si). The enzyme-catalysed hydrolyses were carried out under nitrogen in a pH-stat RTS 822 (Radiometer), using thermostatted vessels. Reactions were monitored by t.l.c. on Silica Gel G (Merck), using chloroform–methanol 100:10 (*A*), 100:5 (*B*), and 100:2 (*C*); and benzene–ethanol 100:10 (*D*), 100:5 (*E*), and 100:1 (*F*). Column chromatography was

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carried out on Silica Gel CH (100–200 μm, Lachema, Brno). The products of enzymic hydrolysis were analysed by g.l.c. after derivatisation (see below) on a column (1200 × 2 mm) of Chromaton N-AW (160–200 μm) containing 15% of butanediol succinate with nitrogen as the carrier-gas at 30 mL/min. A Varian-Aerograph 2100 instrument fitted with a flame-ionisation detector was used, and operated with the column at 200° and the injector and detector at 250°. The peaks were evaluated with a Hewlett–Packard 3380 A integrator.

Porcine liver esterase (EC 3.1.1.1; 200 U/mg of protein) was obtained from Sigma as a suspension in 3.2M $(NH_4)_2SO_4$, containing 8 mg of protein/mL.

Most of the substances studied were prepared from 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose and 1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose[4] by appropriate reaction at position 3, partial hydrolysis of the 5,6-acetal, and acetylation.

3,5,6-Tri-*O*-acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose[5] (**1**), 5,6-di-*O*-acetyl-1,2-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranose[6] (**2**), 3,5,6-tri-*O*-acetyl-1,2-*O*-isopropylidene-α-D-allofuranose[9] (**5**), 3-acetamido-5,6-di-*O*-acetyl-3-deoxy-1,2-*O*-isopropylidene-α-D-allofuranose[11] (**7**), 6-*O*-acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose[12] (**8**), 3-*O*-acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose[3] (**9**), and 6-*O*-acetyl-1,2-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranose[14] (**11**) are known compounds.

3-Acetamido-5,6-di-O-*acetyl-3-deoxy-1,2*-O-*isopropylidene*-α-D-*glucofuranose* (**3**). — Compound **3** was amorphous, $[\alpha]_D^{20}$ +49° (*c* 1, chloroform). The n.m.r. data are given in Tables I and II.

Anal. Calc. for $C_{15}H_{23}NO_8$: C, 52.17; H, 6.71; N, 4.06. Found: C, 51.70; H, 6.49; N, 4.06.

5,6-Di-O-*acetyl-3-deoxy-1,2*-O-*isopropylidene*-α-D-ribo-*hexofuranose* (**4**). — Prepared by acetylation of the 5,6-diol[7,8], **4** had m.p. 54° (from ether–light petroleum), $[\alpha]_D^{20}$ +20° (*c* 0.9, chloroform). The n.m.r. data are given in Tables I and II.

Anal. Calc. for $C_{13}H_{20}O_7$: C, 54.16; H, 6.99. Found: C, 54.45; H, 7.25.

5,6-Di-O-*acetyl-1,2*-O-*isopropylidene-3*-O-*methyl*-α-D-*allofuranose* (**6**). — Prepared by acetylation of the 5,6-diol[10], **6** was a syrup, $[\alpha]_D^{20}$ +107° (*c* 0.6, chloroform). The n.m.r. data are given in Tables I and II.

Anal. Calc. for $C_{14}H_{22}O_8$: C, 52.82; H, 6.97. Found: C, 52.67; H, 7.05.

5-O-*Acetyl-1,2*-O-*isopropylidene-3*-O-*methyl*-α-D-*glucofuranose* (**10**). — Detritylation of **16** by heating in aqueous 80% acetic acid gave a mixture of the 5- (**10**) and the 6-acetate (**11**) in the ratio ~1:1. Column chromatography (chloroform–methanol, 100:1) failed to give pure **10**. Detritylation of **16** with the chlorotrimethylsilane–sodium iodide agent[13] gave a pure 5-acetate **10** (t.l.c., solvent *C*), but its isolation from the reaction mixture always gave a mixture of **10** and **11** (n.m.r. data). The n.m.r. data in Tables I and II were obtained from the spectrum of a mixture of **10** and **11**.

3-Acetamido-6-O-*acetyl-3-deoxy-1,2*-O-*isopropylidene*-α-D-*glucofuranose* (**12**). — Partial enzymic deacetylation of **3** gave **12**, m.p. 142° (from acetone–ether), $[\alpha]_D^{20}$ +40.5° (*c* 0.8, chloroform). The n.m.r. data are given in Tables I and II.

Anal. Calc. for $C_{13}H_{21}NO_7$: C, 51.48; H, 6.98; N, 4.62. Found: C, 51.46; H, 7.00; N, 4.69.

TABLE I

^{1}H-N.m.r. spectra of derivatives of novel 1,2-*O*-isopropylidene-α-D-hexofuranose

Compound	**3**	**4**	**6**	**10**	**12**	**13**	**14**	**15**	**16**
Atom	*Chemical shifts (δ, p.p.m.)*								
H-1	5.884	5.799	5.739	5.883	5.879	5.815	5.778	5.898	5.841
H-2	4.479	4.735	4.687	4.572	4.572	4.766	4.771	4.538	4.534
H-3a	4.662	2.140	3.696	3.714	4.402	2.053	3.802	3.771	3.707
H-3b	–	1.783	–	–	–	1.893	–	–	–
H-4	4.357	4.323	4.053	4.352	4.145	4.243	4.044	4.273	4.569
H-5	5.177	5.174	5.324	5.110	3.935	[a]	4.133	4.171	5.290
H-6a	4.594	4.422	4.369	3.909	4.387	[a]	4.244	3.244	3.427
H-6b	4.060	4.109	4.154	3.783	4.126	[a]	4.104	3.406	3.333
	Coupling constants (Hz)								
$J_{1,2}$	3.5	3.6	3.6	3.8	3.7	3.6	3.6	3.8	3.7
$J_{2,3a}$	0.3	0	4.2	0	0	0	4.2	0	0
$J_{2,3b}$	–	4.5	–	–	–	4.7	–	–	–
$J_{3a,4}$	3.6	4.5	8.9	3.2	3.5	4.6	8.8	3.1	3.1
$J_{3b,4}$	–	10.7	–	–	–	10.7	–	–	–
$J_{4,5}$	9.6	5.5	5.8	8.2	7.7	4.5	3.5	7.3	8.7
$J_{5,6a}$	2.4	3.0	3.1	3.3	2.8	[b]	2.4	4.8	2.2
$J_{5,6b}$	6.3	6.4	7.3	5.0	6.8	[b]	7.7	5.7	5.2
$J_{6a,6b}$	12.2	12.3	12.1	12.0	11.6	[b]	10.8	9.4	10.6

Other data: **3**, δ 1.335, 1.535 (2 s, CMe_2), 1.981 (s, AcN), 2.078, 2.096 (2 s, 2 AcO), 6.404 (d, $J_{3,NH}$ 9.8 Hz, NH); **4**, δ 1.320, 1.509 (2 s, CMe_2), 2.058, 2.084 (2 s, 2 AcO); **6**, δ 1.363, 1.585 (2 s, CMe_2), 2.066, 2.099 (2 s, 2 AcO), 3.463 (s, OMe); **10**, δ 1.322, 1.489 (2 s, CMe_2), 2.090 (s, AcO), 3.300 (s, OH), 3.369 (s, OMe); **12**, δ 1.330, 1.525 (2 s, CMe_2), 2.078 (s, AcN)[c], 2.118 (s, AcO)[c], 4.027 (d, $J_{5,OH}$ 3.0 Hz, OH), 6.534 (d, $J_{3,NH}$ 7.0 Hz, NH); **13**, δ 1.340, 1.533 (2 s, CMe_2), 2.104 (s, AcO), 2.425 (d, $J_{5,OH}$ 2.5 Hz, OH); **14**, δ 1.375, 1.596 (2 s, CMe_2), 2.097 (s, AcO), 2.525 (s, OH), 3.490 (s, OMe); **15**, δ 1.363, 1.529 (2 s, CMe_2), 2.797 (d, $J_{5,OH}$ 5.7 Hz, OH), 3.335 (s, OMe), 7.205–7.461 (m, 15 H, Ph_3C); **16**, δ 1.352, 1.546 (2 s, CMe_2), 2.085 (s, AcO), 3.316 (s, OMe), 7.183–7.453 (m, 15 H, Ph_3C).

[a] Complex multiplet at δ 4.233–4.028. [b] Impossible to read. [c] May be interchanged.

6-O-Acetyl-3-deoxy-1,2-O-isopropylidene-α-D-ribo-hexofuranose (**13**). — Partial enzymic deacetylation of **4** gave **13**, m.p. 48° (from ether–light petroleum), $[\alpha]_D^{20}$ −6.3° (*c* 0.6, chloroform). The n.m.r. data are given in Tables I and II.

Anal. Calc. for $C_{11}H_{18}O_6$: C, 53.65; H, 7.37. Found: C, 53.48; H, 7.55.

6-O-Acetyl-1,2-O-isopropylidene-3-O-methyl-α-D-allofuranose (**14**). — Partial enzymic deacetylation of **6** gave **14**, isolated as a syrup, $[\alpha]_D^{20}$ +65° (*c* 0.7, chloroform). The n.m.r. data are given in Tables I and II.

Anal. Calc. for $C_{12}H_{20}O_7$: C, 52.17; H, 7.30. Found: C, 52.51; H, 7.11.

1,2-O-Isopropylidene-3-O-methyl-6-O-triphenylmethyl-α-D-glucofuranose (**15**). — Trityl chloride (4.45 g, 16 mmol) was added to a solution of 1,2-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranose[6] (3.39 g, 14.5 mmol) in pyridine (40 mL). The mixture was stored at room temperature for 48 h, diluted with ice–water, and extracted with

TABLE II

^{13}C-N.m.r. chemical shifts for solutions in $CDCl_3$

Compound	*Chemical shifts (δ, p.p.m.)*		
	C-1	*C-2–C-5*	*C-6*
3	104.69	84.46, 76.42, 67.75, 54.66[a]	63.86
4	105.59	80.17, 76.40, 71.89, 35.43[a]	62.97
6	104.06	81.95, 76.87, 76.04, 70.73	62.92
10	105.22	83.77, 81.44, 78.33, 71.50	62.11
12	104.26	84.03, 78.25, 67.69, 56.70[a]	65.51
13	105.29	80.62, 78.19, 69.99, 33.18[a]	65.44
14	104.22	79.89, 77.94, 77.18, 69.58	64.90
15	105.03	84.55, 81.51, 79.39, 69.42	65.24
16	105.27	83.72, 81.36, 77.85, 69.99	62.86

Other signals: **3**, δ 170.85[b], 169.99[b], 20.82, 20.72 (2 AcO), 170.04[b], 23.04 (AcN), 112.38, 26.65, 26.17 (CMe_2); **4**, δ 170.61, 170.07, 20.93, 20.75 (2 AcO), 111.50, 26.78, 26.17 (CMe_2); **6**, δ 170.68, 170.31, 20.89, 20.75 (2 AcO), 113.36, 26.82, 26.52 (CMe_2), 57.99 (MeO), **10**, δ 170.14, 20.94 (AcO), 111.75, 26.80, 26.29 (CMe_2), 57.87 (MeO); **12**, δ 171.78[c], 20.88 (AcO), 171.20[c], 23.09 (AcN), 112.31, 26.48, 26.17 (CMe_2); **13**, δ 171.19, 20.85 (AcO), 111.45, 26.78, 26.14 (CMe_2); **14**, δ 171.04, 20.90 (AcO), 113.39, 26.85, 26.54 (CMe_2), 57.98 (MeO); **15**, δ 143.79, 128.95, 128.68, 127.87, 127.08, 86.70 (Ph_3C), 111.60, 26.73, 26.31 (CMe_2), 57.83 (MeO); **16**, δ 171.07, 21.0 (AcO), 144.04, 128.77, 127.82, 127.70, 126.90, 86.29 (Ph_3C), 111.76, 26.81, 26.35 (CMe_2), 57.88 (MeO).

[a] C-3. [b,c] May be interchanged.

chloroform (3 × 30 mL). The combined extracts were dried, the solvent was evaporated, and trityl alcohol was separated by crystallisation from ether or acetone. Column chromatography (solvents *F* and *E*) of the residue then gave **15**, $[\alpha]_D^{20}$ −40° (*c* 1.2, chloroform). The n.m.r. data are given in Tables I and II.

Anal. Calc. for $C_{29}H_{32}O_6$: C, 73.09; H, 6.77. Found: C, 73.42; H, 7.09.

5-O-Acetyl-1,2-O-isopropylidene-3-O-methyl-6-O-triphenylmethyl-α-D-glucofuranose (**16**). — Treatment of **15** (1.8 g, 3.77 mmol) with acetic anhydride (2 mL) in pyridine (20 mL) at room temperature gave **16**, m.p. 157–159° (from ether–light petroleum), $[\alpha]_D^{20}$ −39° (*c* 0.4, chloroform). The n.m.r. data are given in Tables I and II.

Anal. Calc. for $C_{31}H_{34}O_7$: C, 71.80; H, 6.61. Found: C, 71.94; H, 6.71.

The enzyme-catalysed hydrolysis of **1–7**. — (*a*) *Under homogeneous conditions.* To a ~3mM solution (10 mL) of each substrate in 0.5M KCl at 30°, after adjustment of the pH to 7.0 and stirring for 10 min, was added the porcine liver esterase (5 μL, original concentrate diluted 1:20 with water). An initial linear time-dependence of the consumption of 0.01M NaOH necessary to maintain pH 7.0 was observed (5–10 min). The rate of deacetylation was calculated by the relation

$$v = \frac{[\text{consumption (L)} \times \text{concentration (molarity)}]\ \text{NaOH}}{\text{time (min)} \times 0.25}$$

TABLE III

Initial rate of the enzymically catalysed hydrolysis of 1,2-*O*-isopropylidene-α-D-hexofuranose acetates and their solubility in 0.5M KCl

Compound	*Initial rate*[a] (v, *μmol. min*$^{-1}$)		*Solubility* (*mg. mL*$^{-1}$)
	A (100v)	*B (10v)*	
1	2.75	5.12	2.20
2	5.30	12.3	3.78
3	1.17	6.29	20.0
4	2.60	9.84	11.0
5	2.0	6.5	1.98
6	1.75	3.25	5.20
7	1.10	0.20	5.30
8	–	2.16	–
9	–	1.9	–

[a] A, Homogeneous medium; B, heterogeneous medium.

which gives the mol of ester cleaved per min by 1 μL of enzyme. The initial rates are given in Table III (column *A*).

(*b*) *Under heterogeneous conditions.* To a dispersion of each substrate (0.05–0.1 mmol) in 0.5M KCl (2 mL) at 30° and pH 7.0 was added a solution of the porcine liver esterase (100 μL, original concentrate diluted 1:10 with water). The pH was maintained at 7.0 and the consumption of 0.1M NaOH during the first 5–10 min of reaction was used to calculate the initial rates of reaction. The results are given in Table III (column *B*).

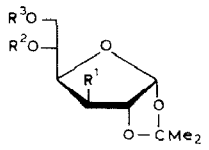
In parallel experiments in (*a*) and (*b*), samples were taken from each reaction mixture, and the components were extracted with chloroform, trimethylsilylated[15], and analysed by g.l.c. with appropriate internal standards.

(*c*) *Preparative hydrolyses.* Each enzymic hydrolysis was carried out in 5 mL of electrolyte with 0.2–0.5 mmol of substrate in the presence of 30–50 μL of the original enzyme concentrate by procedure (*b*). When the reaction was complete, the mixture was extracted with chloroform (3 × 5 mL), the combined extracts were concentrated, and the residue was subjected to column chromatography (solvent *E* at 1 mL/min). After further purification, the substances separated were analysed by ordinary chemical procedures and identified by ^{1}H- and ^{13}C-n.m.r. spectroscopy.

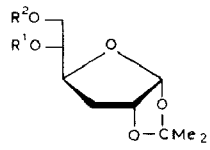
RESULTS AND DISCUSSION

The initial rates of the enzyme-catalysed hydrolyses of **1–7**, which are shown in Table III, were determined under homogeneous (column *A*) and heterogeneous (column *B*) conditions (see Experimental). Only the values in column *A* are considered below. The solubilities of **1–7** in the electrolyte showed no direct dependence on the initial rates.

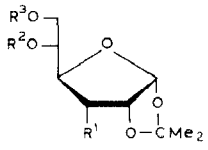
The rate values given in column A are ~ 100 and ~ 1000 times smaller than those



1 R^1 = OAc, R^2 = R^3 = Ac
2 R^1 = OMe, R^2 = R^3 = Ac
3 R^1 = NHAc, R^2 = R^3 = Ac
8 R^1 = OH, R^2 = H, R^3 = Ac
9 R^1 = OAc, R^2 = R^3 = H
10 R^1 = OMe, R^2 = Ac, R^3 = H
11 R^1 = OMe, R^2 = H, R^3 = Ac
12 R^1 = NHAc, R^2 = H, R^3 = Ac
15 R^1 = OMe, R^2 = H, R^3 = Tr
16 R^1 = OMe, R^2 = Ac, R^3 = Tr



4 R^1 = R^2 = Ac
13 R^1 = H, R^2 = Ac



5 R^1 = OAc, R^2 = R^3 = Ac
6 R^1 = OMe, R^2 = R^3 = Ac
7 R^1 = NHAc, R^2 = R^3 = Ac
14 R^1 = OMe, R^2 = H, R^3 = Ac

for the enzymic deacetylation of carbohydrate acetates dealt with so far[1,16], which reflects the low concentrations of enzyme and substrate used in the homogeneous reactions.

Comparison of the rates for the members of the pairs **1/5**, **2/6**, and **3/7** indicates that the *gluco* compounds are more reactive than the *allo* isomers although, with the exception of the pair of 3-methyl ethers **2/6**, the differences in reactivities are small. The effect of the size of the 3-substituent on the initial rate followed the sequence $v_H > v_{OMe} > v_{OAc} > v_{NHAc}$ for the *allo* compounds and the sequence $v_{OMe} > v_{OAc} > v_H > v_{NHAc}$ for the *gluco* compounds.

Partial enzymic hydrolyses of **2–4** and **6** were carried out on a preparative scale and the products were analysed by t.l.c., which revealed small proportions of diols and starting materials but mainly monoacetates, the structures of which, after isolation by chromatography, were determined by ^{1}H-n.m.r. spectroscopy. The monoacetates **11–14** each showed a considerable upfield shift (> 1 p.p.m.) of the signal for H-5 but not for the signals for H-6a and H-6b, compared with those of the corresponding diacetates (**2–4** and **6**). Thus, **11–14** were each identified as a 6-acetate.

The course of the enzymic deacetylation of **1–7** was investigated by g.l.c. of the derivatised samples (see Experimental) and comparison with reference compounds. The complex results for the triacetate **1** are shown in Fig. 1. The triacetate **5** showed a similar course of deacetylation. A much simpler pattern is shown for the diacetate **4** in Fig. 2, which reveals selective hydrolysis of the diacetate and indicates the most advantageous stage of deacetylation for obtaining the 6-acetate. Similar selectivity occurred during the hydrolyses of the acetamido derivatives **3** and **7**. For the diacetates **2** (Fig. 3) and **6**, both monoacetates were detected. For most of the substrates, the rate of hydrolysis decelerated when the main component of the mixture was the monoacetate, which accords with the low initial rates of the enzymic hydrolysis of the monoacetates **8** and **9** (Table III).

The main product of each partial hydrolysis was the 6-acetate, which could arise by selective hydrolysis of the 5-acetate or selective hydrolysis of the 6-acetate followed by a 5→6 acetyl migration. Acetyl migration in partially acetylated polyhydroxyl

compounds is well known[17,18] and tends to occur towards primary positions. Acetyl migration occurs chemically in acid and alkaline media and has been used, for example, to prepare the 6-acetate **8** from the 3-acetate **9** in an alkaline medium[3]. In the absence of enzyme and at pH 7.0, the 6-acetate **8** gave (g.l.c. data) a mixture of **8** (95.5%) and **9** (1.85%) plus other isomers. Likewise, the 3-acetate **9** gave, after 5 min, 82% of the 6-acetate **8**, and, after 6 h, the same equilibrium mixture as obtained from **8**.

For the enzymically catalysed hydrolysis of the 5,6-diacetate **2**, the 5-acetate **10** was the initial main product, but it was progressively replaced by the 6-acetate **11** (Fig. 3). In order to verify the occurrence of acetyl migration in this process, mixtures with

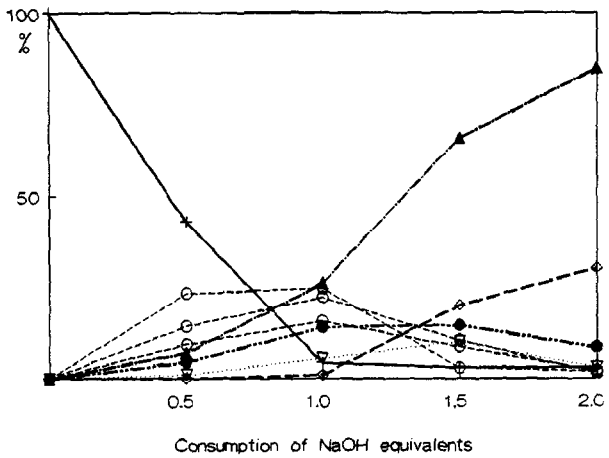


Fig. 1. Enzymic hydrolysis of 3,5,6-tri-*O*-acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose (**1**): +, **1**; ○, diacetates; ▲, 6-acetate; ●, 5-acetate; ▽, 3-acetate; ◇, triol.

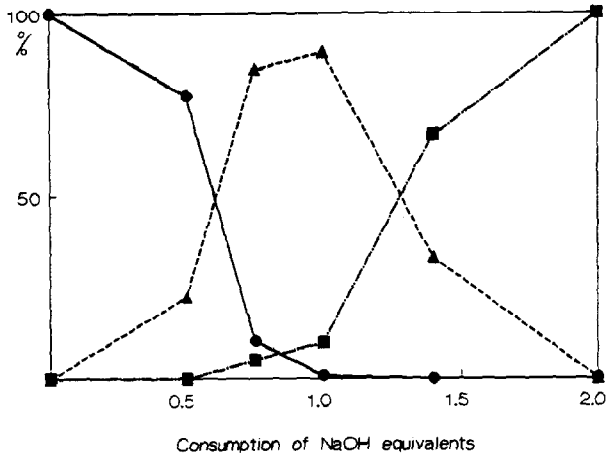


Fig. 2. Enzymic hydrolysis of 5,6-di-*O*-acetyl-3-deoxy-1,2-*O*-isopropylidene-α-D-*ribo*-hexopyranose (**4**): ●, **4**; ▲, **13**; ■, diol.

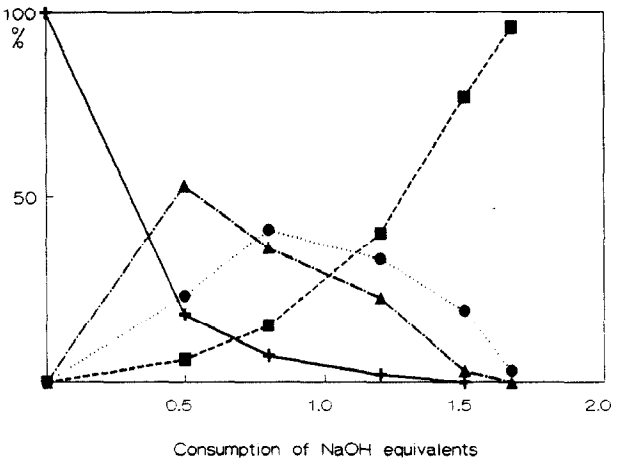


Fig. 3. Enzymic hydrolysis of 5,6-di-*O*-acetyl-1,2-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranose (**2**): +, **2**; ▲, **10**; ●, **11**; ■, diol.

TABLE IV

Changes in the composition of mixtures[a] of the monoacetates **10** and **11** in 0.5M KCl at pH 7.0 in the presence and absence of porcine liver esterase

Time (min)	*With enzyme*[b]		*Without enzyme*		*With enzyme*[b]		*Without enzyme*	
	10 (%)	**11** (%)	**10** (%)	**11** (%)	**10** (%)	**11** (%)	**10** (%)	**11** (%)
0	71.6	28.3	71.6	28.3	15.1	85.0	15.1	85.0
3	–	–	–	–	–	–	14.7	85.6
10	47.5	46.0	10.7	89.6	14.0	84.0	12.5	87.4
40	22.2	67.5	–	–	10.4	81.2	–	–
60	19.2	70.1	9.4	90.6	10.1	78.5	10.3	89.6
120	10.2[c]	67.0[c]	9.6[c]	90.2[c]	8.4[d]	69.0[d]	10.2	89.6
180	7.6	60.7	9.4[e]	90.6[e]	8.1[f]	60.2[f]	10.2	89.6

[a] A solution of each mixture (Σ 26.2 mg, 0.1 mmol) in 0.5M KCl (2 mL) was stirred at pH 7.0 and 25° without and with the enzyme (10 μL). [b] Some 5,6-diol was present also. [c] 130 min. [d] 140 min. [e] 190 min. [f] 210 min.

different proportions of **10** and **11** were used. The changes in composition in the absence and presence of enzyme were then determined; only in the former case could changes occur by acetyl migration. The results, which are given in Table IV, show rapid acetyl migration in the absence of enzyme and the formation of a ~ 1:9 equilibrium mixture of the monoacetates **10** and **11**. In the presence of enzyme, the acetyl migration is slower but yields the same equilibrium mixture. Thus, in the presence of enzyme, the major part of the 5,6-diol is formed from the 6-acetate **11**.

The main products of the partial enzymic deacetylation of the diacetates **2–4** were the 6-acetates, which have potential value in synthesis by providing access to 5-substituted derivatives. The chemical preparation of 6-acetates by partial acetylation of 5,6-diols can give good results[19,20], but partial enzymic hydrolysis of 5,6-diacetates accompanied by 5→6 acetyl migration may be a useful alternative method.

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